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L. Martinson, M. Alveteg, C.-M. Mörth, P. Warfvinge

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Liisa Martinson[1], Mattias Alveteg[1], Carl-Magnus Mörth[2] and Per Warfvinge[1]

[1]Department of Chemical Engineering, Lund University, P.O. Box 124, SE 221 00 Lund, Sweden
[2] Department of Geology and Geochemistry, Stockholm University, SE 106 91 Stockholm, Sweden

Email for corresponding author: liisa.martinson@chemeng.lth.se

Abstract

The multi-layer dynamic soil chemistry SAFE model was used to study the dynamics of recovery in the F1 catchment at Lake Gårdsjön, Sweden. The influence of (1) sulphate adsorption, and (2) changes in marine deposition, on model predictions of recovery was studied. Sulphate adsorption/desorption in SAFE is modeled by an isotherm in which sulphate adsorption is dependent on both the sulphate concentration and the pH in the soil solution. This isotherm was parameterised for the B-horizon of F1 for the sulphate concentration range 10–260 μmol^{-1} and the pH range 3.8–5.0. Sulphate adsorption/desorption as the only soil process involving sulphate is adequate to predict sulphate in run-off at F1. Adding the process caused time-delays in sulphate concentration in run-off of only 1-2 years, which was much shorter than previously seen in the adjacent G1 catchment. The location of Lake Gårdsjön, approximately 15 km inland from the Swedish west coast, ensures that the marine deposition to the area is high. Model output showed that the temporal variation in marine deposition has a considerable impact on the run-off chemistry. Such changes in marine deposition are difficult to foresee and their influence on modelled run-off chemistry can be large when soils start to recover as the previously high concentrations of anthropogenic sulphate in the soil solution decrease.

Keywords: climate change, dynamic modelling, run-off chemistry, sea-salt effect, soil and water acidification, sulphate adsorption

Introduction

Sulphur emissions in Europe increased steadily from the start of industrialisation until the 1970s and have since decreased considerably (Mylona, 1993; Vestreng and Støren, 2000). This successful abatement was largely due to work within the Convention of Long Range Transboundary Air Pollution of the United Nations Economic commission for Europe (UNECE/LRTAP). In Sweden, the total S deposition has decreased by as much as 70% (Westling and Lövblad, 1999). Although sulphate in run-off has decreased at individual sites (Moldan *et al*., 2001), the large reduction in the deposition of S has not yet resulted in any significant decrease in run-off sulphate for the country as a whole, since many catchments in Sweden have a net loss of sulphate due to desorption of inorganic sulphate and mineralisation of organic sulphur (Wilander, 2001).

As acidifying emissions have decreased, the focus of interest has shifted from long-term measures such as exceedence of critical loads to the dynamic behaviour (Munthe *et al*., 2002). In the forthcoming emission reduction protocols (UNECE/LRTAP), more emphasis will, consequently, be put on the temporal aspects of recovery. Thus, increasing the precision in assessing the chemical recovery of terrestrial and aquatic ecosystems is very important.

In aiming to increase the precision in modelling the dynamics of recovery, it is important to identify factors that influence future dynamics. This includes not only focusing on the soil processes that have a large impact on modelling recovery, but also investigating links between the dynamics of recovery from acidification and other important factors, such as a changing climate.

The aim of the present study was to model recovery in the F1 catchment at Lake Gårdsjön in Sweden using the

dynamicsoil chemistry model SAFE and to assess the effect of both natural and anthropogenic deposition changes on the prediction of run-off chemistry. Two aspects were focused on: sulphate adsorption/desorption and changes in marine deposition.

Sulphate adsorption/desorption was recently added to SAFE. An application of the model to the roof-covered site, G1, at Lake Gårdsjön has shown that the prediction of recovery improved considerably when this process was added (Martinson *et al*., 2003). The large difference in deposition dynamics between F1, which was never roof-covered, and G1 makes the Gårdsjön area suitable for comparing the influence of sulphate adsorption/desorption. Furthermore, adsorption/desorption is the only process in the S cycle normally included in dynamic soil chemistry models, e.g. MAGIC (Cosby *et al*., 2001); SMART (Kämäri *et al*., 1995). However, other sulphate processes may also influence the prediction of recovery; mineralisation of organic sulphur may be a source of sulphate in run-off (Mitchell *et al.*, 2001; Alewell *et al*., 1999) and in peaty soils there may be a net retention of sulphate by bacterial dissimilatory sulphate reduction (Gorham *et al*., 1984). F1, but not G1, contains some peaty areas in the central valley, and it is therefore interesting to investigate if sulphate adsorption/desorption alone is adequate to predict sulphate in run-off from F1.

Lake Gårdsjön lies in an area where sea-salt deposition is a high and important part of the base cation deposition (Ferm and Hultberg, 1998). The temporal variation in sea-salt deposition is considerable because of variations in the frequency and intensity of mid latitude cyclones (Gustafsson and Hallgren-Larsson, 2000b). Several recent studies point out the importance of the 'sea-salt' effect when modelling recovery (Evans *et al*., 2001; Skjelkvåle *et al*., 2003; Beier *et al*., 2003). In a changing climate, sea-salt episodes are likely to become more frequent. These can lead to sudden acid surges in areas with acidified soils because the high inputs of Na^+ will exchange for inorganic Al^{3+} and H^+ on cation exchange sites. Since Na^+ does not take part in cation exchange in SAFE, the sea-salt effect cannot be fully modelled using this model. However, sudden changes in marine deposition will still affect the prediction of recovery by SAFE, and these effects are here discussed by using two scenarios.

Materials and Methods

MODEL DESCRIPTION

SAFE is a dynamic multi-layer soil chemistry model. It includes process-oriented descriptions of cation exchange reactions, chemical weathering of minerals, solution equilibrium reactions involving carbon dioxide, organic acids and Al-species as well as leaching and accumulation of dissolved chemical components. The model requires layer-specific chemical and physical parameters and time-series of input data regarding atmospheric deposition, net uptake of nutrients, litter-fall, canopy exchange, net mineralisation and precipitation. In SAFE, the base cations are defined as the sum of Ca^{2+}, Mg^{2+} and K^+. Detailed descriptions of the model can be found in Warfvinge *et al*., 1993) and Alveteg (2003).

In a recent modification of the model, sulphate adsorption was added (Martinson *et al*., 2003). Sulphate adsorption/desorption in the model is described by the empirical pH and sulphate concentration dependent isotherm:

$$\mathrm{ads}SO_4 = q[SO_4^{2-}]^n [H^+]^m \quad (1)$$

where $\mathrm{ads}SO_4$ is expressed in mol kg^{-1} field moist soil and the concentrations of SO_4^{2-} and H^+ are expressed in mol L^{-1}.

In this model, adsorption of sulphate may be accompanied by neutralisation of hydrogen ions. To charge-balance sulphate equally, the number of hydrogen ions neutralised with every sulphate ion, η, should be 2. Experimental studies have shown that the correct number is slightly less than 2 in low ionic strength soil systems (Gustafsson, 1995). Measurements on Swedish forest soil at pH 4.6–4.7 and sulphate concentrations of 100–400 μmol L^{-1} have shown that η is close to 1.7 (Karltun, 1997). In SAFE, this parameter has to be set in the range ($1 \leq \eta \leq 2$). Hence four parameters q, m, n and η are needed to model sulphate adsorption. The isotherm parameters can be determined by a series of batch experiments, which should span the pH and sulphate concentration ranges observed at the site.

SITE DESCRIPTION

The Lake Gårdsjön area is located in southwest Sweden, 50 km north of Göteborg and 15 km inland from the coast (58°03′ N, 12°01′ E). Studies of the effects of acidification and its reversal in the Lake Gårdsjön area started in the 1970s and have been ongoing since (Andersson, 1985; Hultberg and Skeffington, 1998). Between 1991 and 2001 the subcatchment, G1 (0.63 ha) was roof-covered and the adjacent subcatchment F1 was chosen as a reference plot. The area of F1 is 3.7 ha and the vegetation consists mainly of Norway Spruce (*Picea abies*) and some Scots Pine (*Pinus sylvestris*). The ground vegetation consists mainly of dwarf shrubs (*Vaccinium myrtillus*) and grass (*Deschampsia flexuosa*). The average soil depth in F1 is 0.68 m (Andersson

et al., 1998) and the soil is classified as an orthic ferro-humic podzol according to the Canadian system (Andersson *et al*., 1998). Part of the F1 catchment consists of peaty soil, which may be of importance when investigating sulphate dynamics.

DATA

Soil, vegetation and deposition data

The data used in this model application (Table 1) are from a previous application of SAFE to the F1 site at Lake Gårdsjön by Sverdrup *et al.* (1998) except for the extra parameters needed for modeling sulphate adsorption. Time series of

Table 1. Soil data for the F1 catchment at Lake Gårdsjön used as input to SAFE.

Parameter	*Unit*	*Soil layer*			
		1	*2*	*3*	*4*
Morphological characterisation		O	A/E	B	B/C
Soil layer thickness	m	0.09	0.06	0.30	0.23
Vol. soil water content	$m^3 m^{-3}$	0.15	0.25	0.30	0.35
Soil bulk density	$kg\ m^{-3}$	300	800	700	1250
Specific surface area	$m^2m^{-3}\ .10^{-6}$	0.48	1.2	1.1	1.98
Cation exchange capacity	$keq\ kg^{-1}.10^6$	352	22	61	13
CO_2 pressure	times ambient	2	5	20	30
Dissolved organic carbon	$mg\ L^{-1}$	35	30	10	5
kGibb	-	6.5	7.5	8.5	9.5
Inflow	% of precipitation	100	70	55	50
Outflow	% of precipitation	70	55	50	50
BC Uptake	% of total	50	40	10	0
N uptake	% of total	50	40	10	0
SULPHATE ADSORPTION PARAMETERS:					
q	-	-	-	0.014	-
m	-	-	-	0.10	-
n	-	-	-	0.14	-
η	-	-	-	1.7	-
MINERALS:	% of total				
K-feldspar		15	15	18	19
Plagioclase		14	14	15	16
Albite		0	0	0	0
Hornblende		0.1	0.5	1.5	1.5
Pyroxene		0	0	0	0
Epidote		0.1	0.5	0.75	1.0
Garnet		0	0.1	0.1	0.1
Biotite		0	0.5	0.5	0.5
Muscovite		0	0	0	0
Chlorite		0	0.4	0.4	0.4
Vermiculite		0	3	15	5
Apatite		0	0.1	0.2	0.3

deposition, nutrient cycling and uptake were derived using the MAKEDEP model (Alveteg *et al*., 2002). Deposition numbers used for input to MAKEDEP were taken from Moldan *et al.* (1998) and Ferm and Hultberg (1998). The non-marine part of the wet deposition was scaled to deposition trend curves. Dry deposition in MAKEDEP is scaled with canopy volume. The trend curves of SO_2, NH_4 and NO_x used in MAKEDEP were updated for the years 1965–2010 with trends for this area from Ferrier *et al*. (2001). The future deposition scenario from 2010 onwards is based on the LRTAP Gothenburg Protocol (UN/ECE, 1999).

Experimental determination of adsorption parameters

Soil samples from the A and B horizons were collected from two pits in the F1 catchment, one from the central valley, which is the discharge area, and one from the upper slope of the catchment. All samples were analysed according to the description below. The sample taken from the central valley was considered to have a dominant influence on the run-off and was thus used for parameterising the isotherm.

All samples were sieved through a 2 mm steel mesh prior to analysis. The soil samples (wet soil) were extracted with a 0.04 M $NaHCO_3$ solution to release the exchangeable sulphate in the soil (Van Stempvoort *et al*., 1990). The samples were centrifuged at 3500 rpm and the supernatant recovered and analysed. Sodium pyrophosphate extractable, and acid oxalate extractable Al and Fe were measured according to ISRIC (1995). The pH (H_2O) of the soil was measured at a soil:water ratio of 1:2.5 (ISRIC,1995). Total S, Fe and Al were analysed on an ICP-OES, Varian Vista Pro Ax system. Sulphate and chloride were analysed with a Dionex DX-300 system.

The sulphate adsorption parameters were determined by a series of batch experiments at six sulphate concentrations (10, 50, 110, 150, 210 and 260 µmol L^{-1}) and five pH levels (3.8, 4.0, 4.3, 4.5 and 5.0), according to the method described in Martinson *et al.* (2003).

The total amount of adsorbed sulphate at every pH and sulphate concentration was calculated as the amount extracted with $NaHCO_3$ plus/minus the amount removed from/released to solution in the batch experiments.

Results and discussion

SOIL ANALYSIS

The largest $NaHCO_3$ extractable amount of sulphate in F1, 1.2 µmol g^{-1}, was found in the B-horizon in the central valley. This was double the amount in the upper slope, 0.52 µmol g^{-1} (Table 2). These amounts were much lower than those previously found in G1, where the adsorbed pool in the B-horizon was 3.4 µmol g^{-1}. To be able to compare differences in soil characteristics, which may influence sulphate adsorption, data from G1 have been included in the comparison. The pH (H_2O) was 4.59 and 4.40 in the A-horizon of the two F1 pits as compared to 4.81 and 4.72 in the B-horizons.

The pyrophosphate extractable Al pool (Al_p) was largest for the G1 samples. In the B-horizon it was approximately 300 µmol g^{-1}, which was almost three times as high as the largest amount in F1. In the A-horizon Al_p was far lower for both catchments. The highest oxalate extractable Al pool (Al_{ox}) was approximately 200 µmol g^{-1} in the B-horizon of G1, approximately 86 µmol g^{-1} in B-horizon of F1 and was low in the A-horizons of both catchments. The differences in pyrophosphate and oxalate extractable Fe pools between the catchments were less pronounced.

Sulphate in soils is sorbed to oxides of Fe and Al (Singh, 1984). The results in this study are no exception; a high positive correlation was found between the pyrophosphate and oxalate extractable pools of Al and the exchangeable pool of sulphate. From the extractions, it was concluded that the main part of the adsorption occurs in the B-horizon and the isotherm was parameterised for this layer only. The difference in soil characteristics between pits shows that

Table 2. Important soil parameters determining sulphate adsorption for two pits in F1, one from the upper slope of the catchment and one from the central valley. For comparison, data from the adjacent G1 catchment has been included.

Site		*F1*		*F1*		*G1*	
		central valley		*upper slope*			
Horizon		*A*	*B*	*A*	*B*	*A*	*B*
pH(H_2O)		4.59	4.81	4.40	4.72	4.17	4.71
extr SO_4^{2-}	µmol g^{-1}	0.041	1.2	0.067	0.52	0.22	3.4
Al_p	µmol g^{-1}	9.5	77.6	33.3	108	24.3	303
Fe_p	µmol g^{-1}	17.7	61.9	31.1	88.7	43.8	81.4
Al_{ox}	µmol g^{-1}	17.3	68.7	36.5	86.4	22.8	200
Fe_{ox}	µmol g^{-1}	27.2	86.4	64.7	108	71.0	58.9

the variability of sulphate adsorption is large; this illustrates the need for soil sampling instead of using a general assumption of sulphate adsorption.

PARAMETERISATION OF THE SULPHATE ADSORPTION ISOTHERM

In the batch experiments, adsorption of sulphate increased with increasing sulphate concentration and decreasing pH down to pH = 4, after which the adsorption was fairly constant (Table 3).

Using the results from the batch experiments, the isotherm for the B-horizon in F1 was parameterised as follows:

$$\mathrm{adsSO_4} = \begin{cases} 0.014\,[\mathrm{SO_4^{2-}}]^{0.10}\,[\mathrm{H^+}]^{0.14} & 4.0 \le \mathrm{pH} \le 5.0 \\ 0.0037[\mathrm{SO_4^{2-}}]^{0.10} & 3.8 \le \mathrm{pH} \le 4.0 \end{cases} \quad (2)$$

where $\mathrm{adsSO_4}$ is expressed in mol $\mathrm{kg^{-1}}$ field moist soil and the concentrations of $\mathrm{SO_4^{2-}}$ and $\mathrm{H^+}$ are in mol $\mathrm{L^{-1}}$. As a measure of goodness-of-fit, the error between measured and calculated adsorption, using the isotherm, was determined. For the point with the largest discrepancy, this error was 13% and the average discrepancy, for all measurements included in the parameterisation, was 3.2%.

The resulting isotherm at different sulphate concentration levels at pH 4.3 for F1, compared to that of G1 (Martinson *et al.*,2003), suggests that there are large differences in sulphate adsorption capacity between the catchments (Fig. 1).

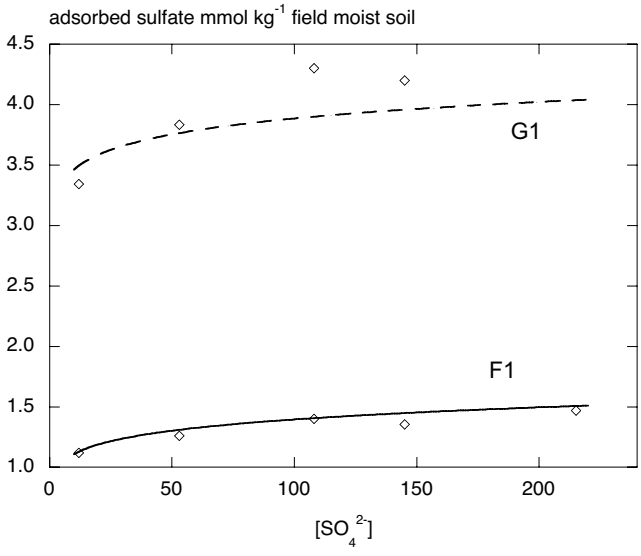

Fig. 1. *A comparison of the resulting isotherm at pH 4.3 for the two catchments, G1(dashed line) and F1(filled line) at Lake Gårdsjön together with batch experiment data for pH 4.3 for both catchments. The G1 data is from Martinson* et al. *(2003).*

Table 3. Adsorbed sulphate in µmol $\mathrm{g^{-1}}$ field moist soil at different pH and sulphate concentration levels from batch experiments.

$[SO_4^{2-}]$	*pH*				
µmol $\mathrm{L^{-1}}$	3.8	4.0	4.3	4.5	5.0
10	-	1.19	1.12	1.09	0.76
50	1.35	1.29	1.26	1.18	-
110	1.51	1.47	1.40	1.38	1.06
150	1.51	1.49	1.35	1.23	1.05
210	1.68	1.61	1.47	1.33	1.12
260	1.75	1.66	-	1.42	1.17

MODEL OUTPUT

Base case

The base case is straightforward use of MAKEDEP to construct time-series of input data for SAFE. Modelled sulphate concentration in run-off clearly follows the trend in measurements (Fig. 2). For the years 1996–1999 the model slightly overestimates the sulphate concentration in run-off. The base cation concentration (i.e. the sum of $[\mathrm{Ca^{2+}}]$, $[\mathrm{Mg^{2+}}]$ and $[\mathrm{K^+}]$) follows measured trends in run-off but the modelled acid neutralising capacity, ANC, is much lower than the ANC calculated from measured concentrations. Nitrate in run-off is negligible for both model predictions and measurements, but there are large differences in the modelled and measured chloride concentration in run-off. In the model, the only source of chloride is wet and dry deposition and there are no soil processes in which chloride takes part. In MAKEDEP dry deposition is scaled according to canopy volume and using this standardised method, sea-salt events cannot be reconstructed. Thus, a sudden change in chloride concentration levels in run-off, such as is seen in the measurements, will not be predicted by SAFE.

Changed sea-salt deposition

After a heavy storm in 1993 severe short-term acidification of run-off was reported in Norway (Hindar *et al*., 1995). Elevated sea-salt deposition was also found in the Lake Gårdsjön area in 1989 (Hultberg and Grennfelt, 1992). A comparison of chloride concentration with lakes in the coastal areas in southwest Sweden confirms that the chloride concentrations in the early 1990s were higher than in the late 1990s (Fig. 3).

In SAFE, $\mathrm{Na^+}$, the dominating cation in sea-salt, does not take part in ion exchange, it only influences ionic strength in the soil solution. Thus, the short-term acidification of run-off from already acidified soils, caused by the 'sea-salt' effect, cannot be fully modelled. However, a sudden change in sea-salt deposition will still affect the modelling of recovery. In the base case, deposition data from the early

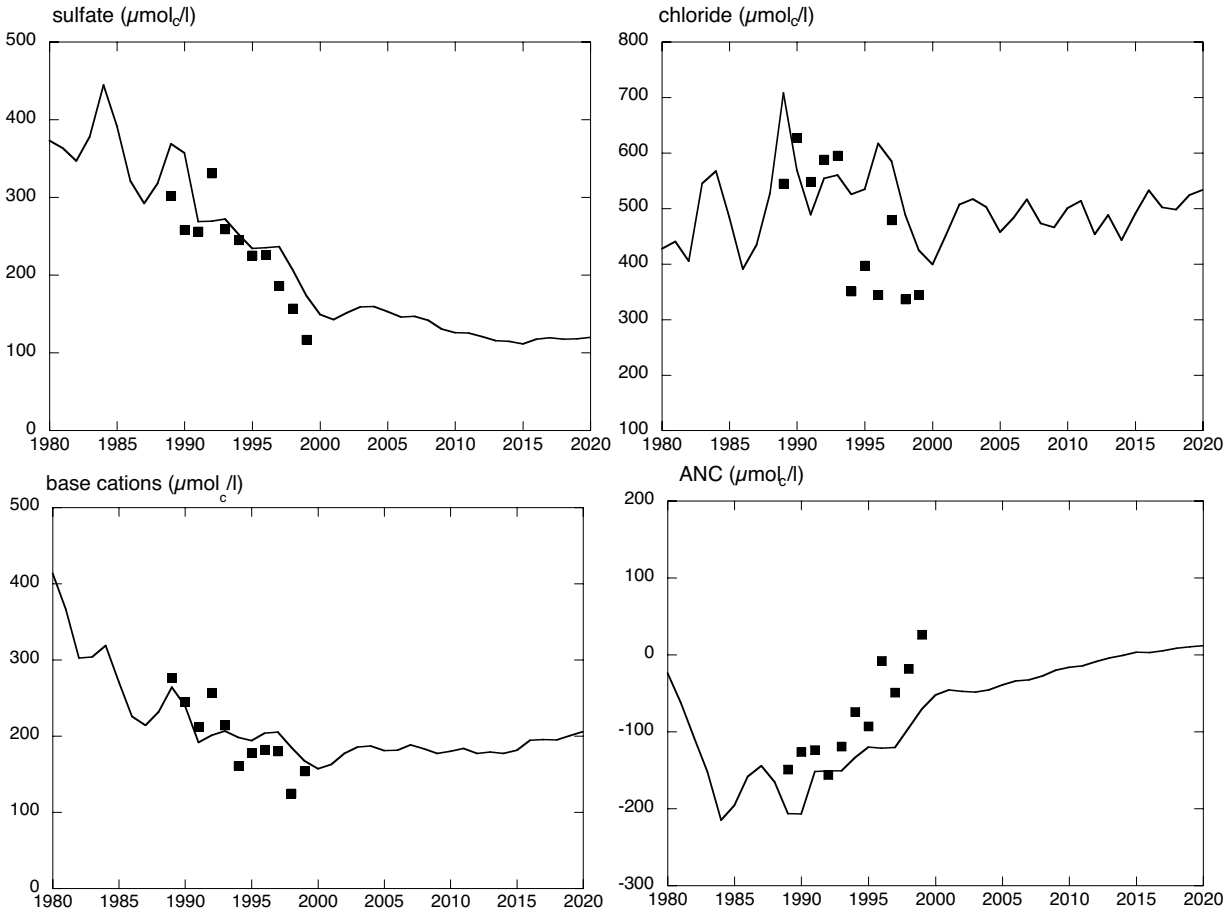

Fig. 2. *The base case. Modelled sulphate concentration, ANC, base cation concentration and chloride concentration in run-off at F1 using SAFE compared to mean annual measurements at the site.*

1990s was used and scaled to trends using MAKEDEP, which led to an overestimation of marine input. To investigate the influence of the change in sea-salt input between the early and late 1990s, the chloride deposition data were re-constructed so that two chloride run-off concentration levels, one 'high' and one 'low' were reached during the 1990s. The deposition of the remaining sea-salt ions was changed accordingly, thus the ANC of the deposition was not changed. Modelled sulphate and base cation concentration in run-off decreased and model predictions improved slightly compared to measurements (Fig. 4). Although both the base cation and sulphate concentration decreased, the increase in ANC was larger and therefore more in accordance with measurements when the sea-salt deposition was lowered.

The ANC in this system is defined as:

$$\mathrm{ANC} = \underbrace{[\mathrm{K^+}] + 2[\mathrm{Mg^{2+}}] + 2[\mathrm{Ca^{2+}}] + [\mathrm{Na^+}]}_{\mathrm{BC}} - \underbrace{2[\mathrm{SO_4^{2-}}] - [\mathrm{Cl^-}] - [\mathrm{NO_3^-}]}_{\mathrm{SAA}} \quad (3)$$

In this case, both BC and SAA decreased due to the lowering of marine input. However, BC in run-off decreased less than SAA. This can be explained by the slower increase in base saturation, when the soil solution concentration of base cations became lower due to the decreased sea-salt deposition (Fig. 5).

The base saturation in the bottom layers at Lake Gårdsjön is fairly low and it is probable that had cation exchange of Na^+ been included in SAFE, the years of high-input of sea-salt would have caused acidification of run-off due to exchange of H^+ and Al^{3+}. At the same time, base saturation of Na^+ would increase. The step decrease of deposition used in this study, would thus have been expected to have an even larger influence on ANC; Na^+, previously stored on the exchange sites in the soil, would have been released to soil solution and the ANC increased. An application of MAGIC to Lake Gårdsjön by Beier *et al.* (2003) similarly showed that a high input of marine deposition caused acidification of run-off in the short term and that base saturation, including Na^+, increased slowly.

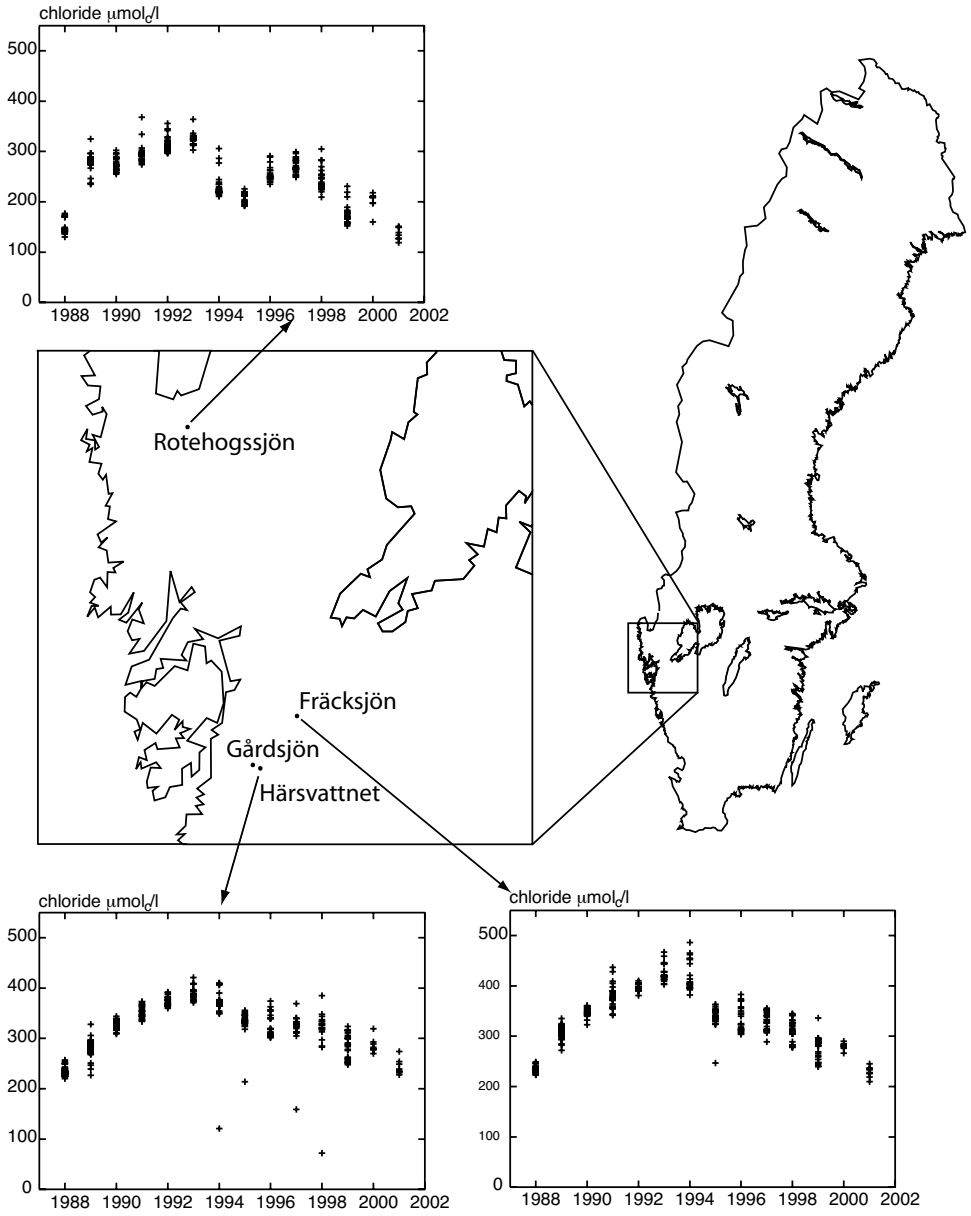

Fig. 3. *The location of Lake Gårdsjön, and the chloride concentration between 1988–2001 in three monitored lakes in the vicinity. The data is provided by the Swedish Environmental Protection Agency and the Department of Environmental Assessment, Swedish Agricultural University, Uppsala, and publicly available on http://www.ma.slu.se}*

A calculation of the mean absolute difference between the measurements and the two model simulations, i.e. the base case and the case of changed marine deposition respectively, for the years 1989–1999, shows that model predictions of ANC, base cations and sulphate improved when the marine deposition was changed (Table 4). The influence was negligible for sulphate but of importance for model predictions of ANC.

Table 4. The mean absolute value of the difference between model calculated values and measurements at F1, Lake Gårdsjön in $\mu mol_c\ l^{-1}$ for the years 1989–1999. Both the base case and the case of changed sea-salt deposition are compared to measured values.

	ANC	*base cations*	SO_4^{2-}	Cl^-
Base case	59.0	25.0	39.5	115
Changed sea-salt dep	44.5	15.2	33.9	41.4

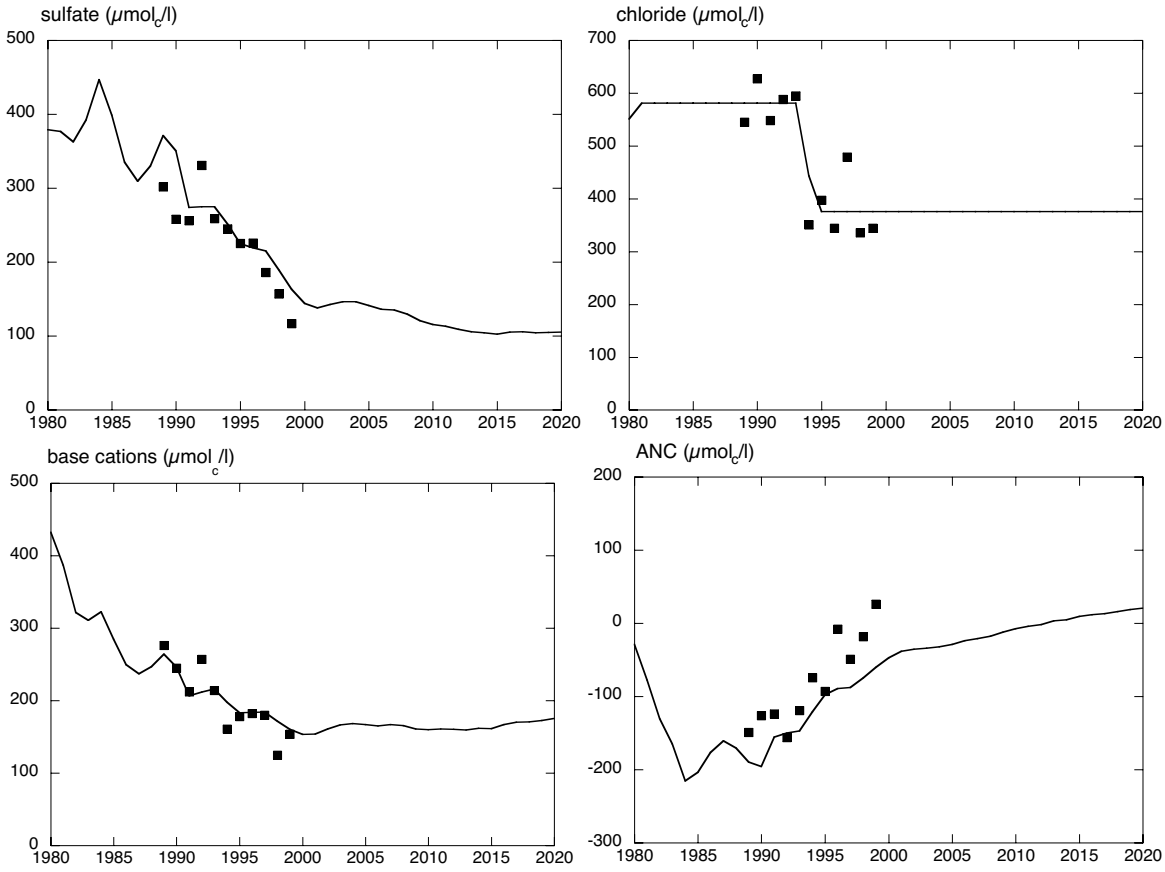

Fig. 4. *Changed marine deposition. Modelled sulphate concentration, ANC, base cation concentration and chloride concentration in run-off compared to mean annual measurements at the site.*

Sulphate dynamics

The differences in the model prediction of sulphate in run-off for the base case and in the case of changed sea-salt deposition are not large. In both cases, the model slightly overestimates the run-off sulphate concentration. As approximately 10% of the catchment area is peaty, it may be that, under such conditions, sulphate reduction can be a net sink of sulphate. Studies at the F1 catchment at Lake Gårdsjön have shown that dissimilatory sulphate reduction is ongoing and approximations show that as much as 3–8% of the total sulphur flux is retained (Morth, 1999).

The modelled exchangeable pool of sulphate in F1 reaches a maximum of 330 mmol$_c$ m^{-2} (Fig. 6), based on a soil bulk density of 700 kg m^{-3} and depth of the B-horizon of 0.3 m (Sverdrup *et al*., 1998). Compared to G1, the level of the exchangeable pool in F1 is much lower (Martinson *et al*., 2003). Furthermore, the drastic deposition cut caused by covering G1 was not seen in F1, although a considerable deposition decrease took place more slowly during a 10-year period in F1.

Although the above decrease in sea-salt deposition changed the ANC and thus the pH in soil solution, its effect on sulphate adsorption was very limited. The adsorbed pool decreased by a maximum of 3% for the changed sea-salt scenario.

To evaluate the effect of a sudden change of acidifying deposition a roof was 'constructed' over F1 in the model simulations, i.e. the deposition under the G1 roof for the years 1991–2001 was used for F1. The model was run with and without sulphate adsorption for this case and compared to model runs with and without sulphate adsorption for the normal (i.e. no roof) case (Fig. 7). In the normal case, the differences between model runs with and without sulphate adsorption were not significant; adding sulphate adsorption/desorption reduced the temporal variability of sulphate concentration slightly and there was a time lag between model runs of approximately one to two years. This time lag increased, up to five years, for the case when a roof was 'constructed'. For G1, where the adsorption capacity was larger, the time-lag was between five and ten years (Martinson *et al*. 2003).

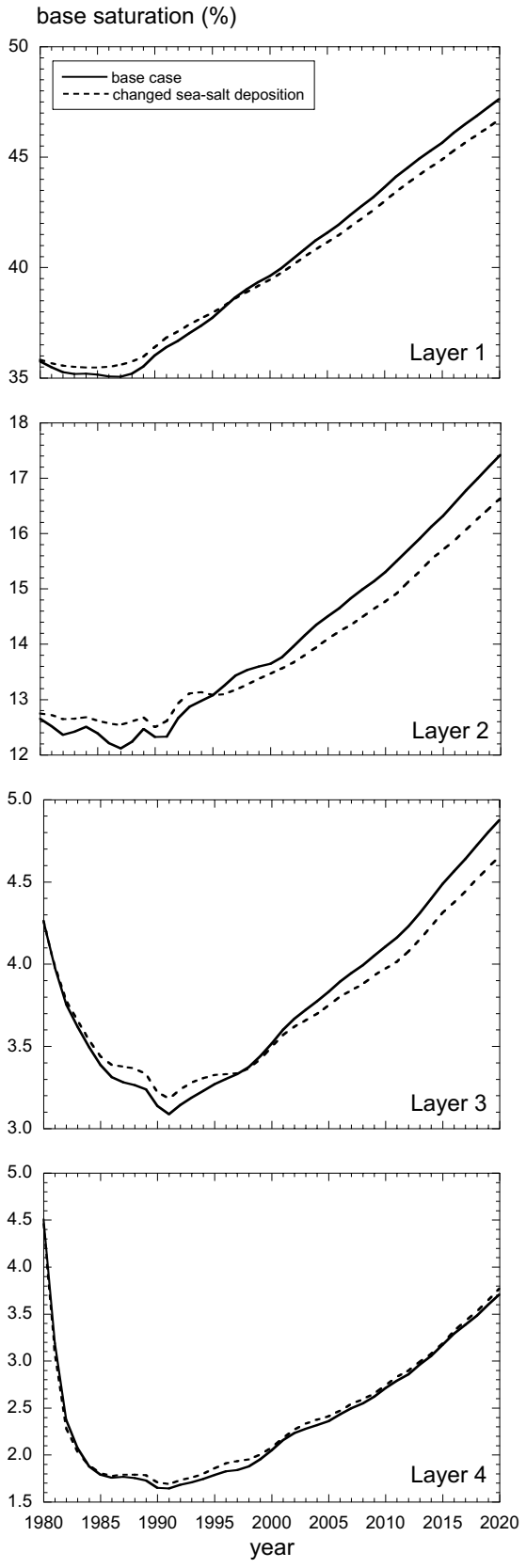

Fig. 5. *A comparison of base saturation in the different soil layers using the two sea-salt deposition scenarios.*

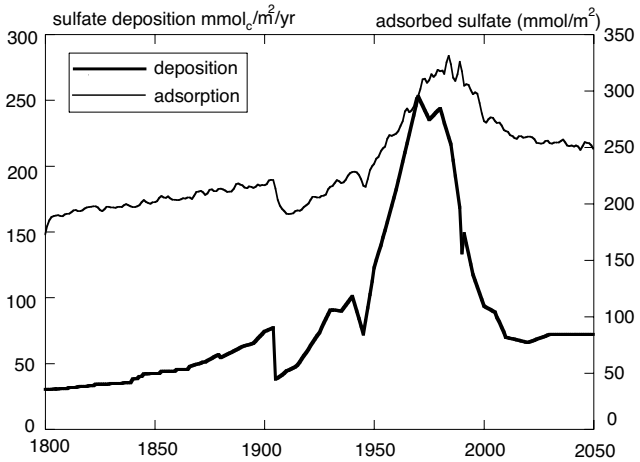

Fig. 6. *Modelled sulphate adsorption at F1 compared to the sulphate deposition used in the model.*

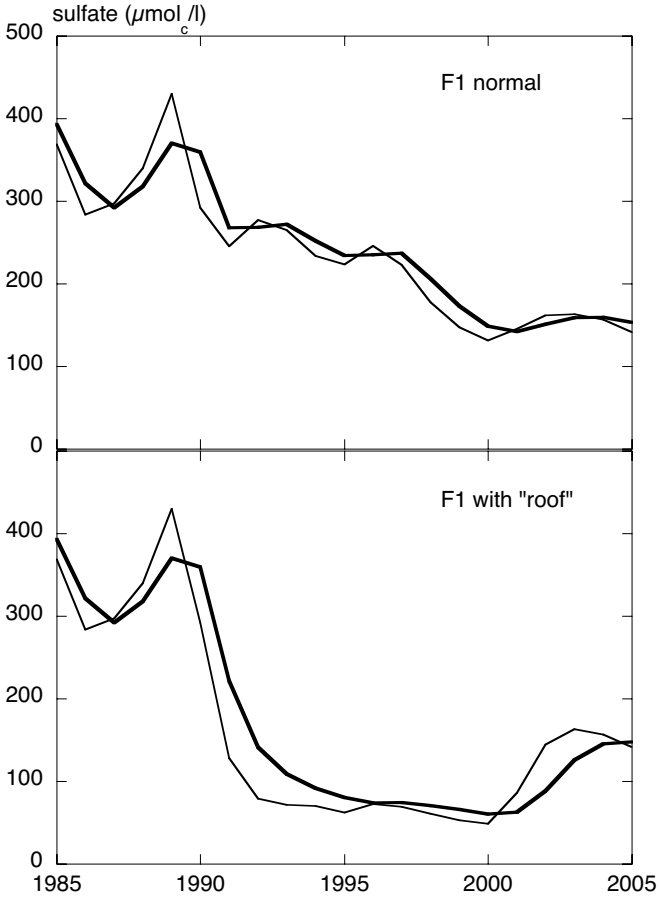

Fig. 7. *Modelled sulphate concentration in run-off, using SAFE with (coarse line) and without (fine line) sulphate adsorption/ desorption. In the bottom figure it is assumed that a roof was constructed over F1.*

Conclusions

Applying SAFE with sulphate adsorption/desorption to the roof-covered catchment G1 at Lake Gårdsjön considerably increased the precision in modelling recovery (Martinson *et al*., 2003). In the present study, where the model was applied to the control catchment F1, the influence of adsorption on recovery was limited. This difference between the sites depends both on differences in deposition dynamics as well as on the amount of exchangeable sulphate in the soil.

The importance of sulphate dynamics for the recovery of soils has been pointed out earlier, e.g. within the RECOVER project (Prechtel *et al.*, 2001), a project in which the F1 catchment at Lake Gårdsjön was one of the sites studied. The present application of SAFE to F1 and the previous application to G1 (Martinson *et al*., 2003) show that including sulphate adsorption/desorption as the only sulphate process in the model is adequate for the temporal resolution studied. The two applications of SAFE to Lake Gårdsjön illustrate how the magnitude of sulphate adsorption for a specific site can be determined successfully by simple experimental studies combined with modelling. However, the results of the applications also illustrate the dangers in assuming a certain adsorption capacity without experimental determination.

The time-delay in recovery when adding sulphate adsorption/desorption to SAFE was seen only during a limited time period, one to two years for F1 and five to ten for G1 (Martinson *et al.*, 2003). Similar results from monitoring run-off chemistry in Scandinavian soils were reported by Moldan *et al*. (2001). They also concluded that this short delay time is characteristic for well-drained soils developed since the last glaciation, that have low adsorption capacities, and that a far longer delay time could be expected in highly weathered soils. Thus, the effect of including sulphate adsorption/desorption to SAFE remains to be investigated when modelling recovery dynamics in areas where soils have a higher sulphate exchange capacity and where deposition levels are higher than in Scandinavia e.g. Central Europe and Asia.

It should also be borne in mind that in a longer time perspective there might be a small but remaining discrepancy between the sulphate concentration predicted by SAFE and the actual sulphate concentration due to sulphur processes not included in the model, e.g. mineralisation of the organic sulphur pool.

The increased precision in modelling recovery by adding sulphate adsorption/desorption was counteracted by changes in sea-salt deposition. Changes in marine deposition due to variations in climate influenced run-off chemistry quite significantly. These changes are difficult to foresee and they are neglected when using a systematic reconstruction method, such as MAKEDEP.

In conclusion, the necessity of including sulphate adsorption/desorption when using SAFE depends both on the soil type and the time scale of interest. When rapid dynamics following deposition cuts are of interest, it is important to include sulphate adsorption/desorption. If the aim is to assess recovery status decades ahead, it may not be necessary. Furthermore, climate-driven changes, e.g. increased storm frequencies, can have a large influence on model predictions of recovery from acidification when the concentrations of anthropogenic sulfate in soils decrease due to reduced sulfur emissions.

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